

nium ion is smaller than the stabilization afforded by the interaction of the charge with the polarizable hydrocarbon framework. Again, the ion is internally solvated in the gas phase.

(4) The above results permit semiquantitative estimates of relative enthalpies of solvation for carbonium ions in HSO_3F . Relevant data for several ions are summarized in Table I.

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(25) National Science Foundation Undergraduate Research Program participant, Summer, 1974.

(26) Camille and Henry Dreyfus Teacher-Scholar, 1971-1976.

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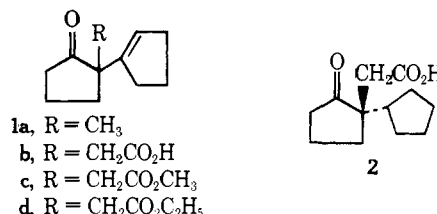
Received July 29, 1974

Stereospecificity in Triplet State Photorearrangements. The Oxa-di- π -methane Photorearrangement.¹ Mechanistic Studies in Photochemistry²

Sir:

Photorearrangements of β,γ -unsaturated ketones have been characterized as either 1,3-acyl migrations or oxa-di- π -methane rearrangements.³ A number of studies have shown that the former occurs by an excited singlet $\pi 2_s + \sigma 2_s$ migration (or its equivalent).⁴ The oxa-di- π -methane rearrangement has also been established as an excited state triplet reaction.⁵ However, the stereochemical consequences of this reaction have not been fully characterized. Several studies have appeared which purport to determine the stereochemical results but the conclusions are contradictory, in one case suggesting a $\pi 2_s + \sigma 2_s$ pathway⁶ while other reports suggest a $\pi 2_a + \sigma 2_a$ rearrangement.⁷ These studies have been carried out on β,γ -unsaturated ketones in which secondary factors (e.g., steric hindrance) may exert a significant or perhaps controlling influence on the course of the rearrangement.

In order to minimize secondary factors and to assure the occurrence of an oxa-di- π -methane rearrangement, we have constructed the model system, 2-(1-cyclopentenyl)-2-methylcyclopentanone (**1a**) and its derivatives,⁸ in order to test the stereochemical consequences at carbon-2 (C-2).⁹ The photorearrangements of **1** under direct or acetone-sensitized conditions are unexceptional and isolated product yields are very good,¹⁰ permitting a thorough mechanistic investigation.



The keto acid **1b** was resolved as the cinchonidine salt into its optical antipodes, and the configurations of the derived carboxylic acids were assigned as (*S*)-**1b** ($[\alpha]^{28\text{D}} + 139^\circ$) and (*R*)-**1b** ($[\alpha]^{28\text{D}} - 138^\circ$) by correlation of the Cotton effects of their CD spectra with the modified octant rule for β,γ -unsaturated ketones¹¹ and the application of the octant rule for the Cotton effect of the saturated derivative (**2**), the carbon-carbon double bond reduction product of (*R*)-**1b** (Table I). Greater than 90% optical purities of the individual enantiomers were demonstrated by use of the chiral shift reagent, *tris*(3-heptafluoropropylhydroxymethylene-d-camphorato)europium(III)¹² with the derived methyl esters (**1c**).

Examination of the direct irradiation product of each of the enantiomeric acids confirmed that a stereospecific 1,3-acyl migration occurred consistent with a 1,3-sigmatropic ($\pi 2_s + \sigma 2_s$) mechanism.⁴ The optical purities of the products

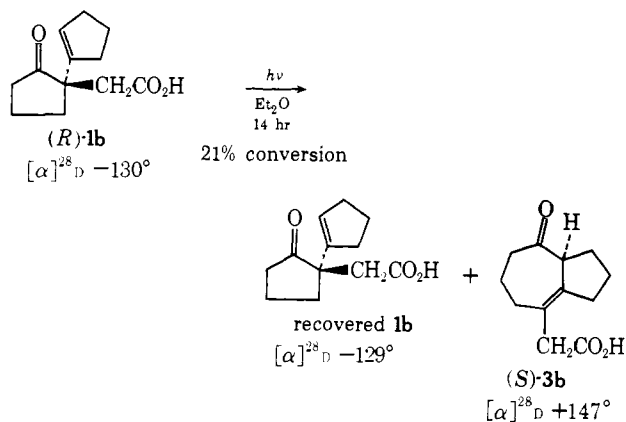
Table I. Specific Rotations, ORD, and CD Results for Ketones 1-5

Enantiomer	Config at α -carbon	$[\alpha]^{28D^a}$	CD or ORD ^c
(+)- 1b	S	+131	$[\theta]_{300} = +8381$ $[\theta]_{214} = -9713$
(-)- 1b	R	-130	$[\theta]_{300} = -8686$ $[\theta]_{214} = +9996$
(-)- 2 (reduction product of (-)- 1b)	R	-67	$[\Phi]_{314} = -1988$ $[\Phi]_{291} = 0$ $[\Phi]_{270} = +1626$
(+)- 3b	S	+140	$[\Phi]_{314} = 12,245$ $[\Phi]_{305} = 11,407$ $[\Phi]_{292} = 0$ $[\Phi]_{263} = -14,762$
(-)- 3b	R	-128	$[\Phi]_{314} = -9651$ $[\Phi]_{305} = -8985$ $[\Phi]_{292} = 0$ $[\Phi]_{263} = 11,814$
(+)- 4b	S	+52	$[\theta]_{318} = 158, [\theta]_{308} = 33$ $[\theta]_{300} = -211, [\theta]_{290} = -330$ $[\theta]_{210} = >10,706^b$
(-)- 4b	R	-47	$[\theta]_{318} = -153, [\theta]_{308} = -15$ $[\theta]_{300} = 229, [\theta]_{290} = 337$ $[\theta]_{210} = <8411^b$
(+)- 5 ¹⁶	S	+147	$[\theta]_{287} = 9060$ $[\theta]_{214} = 11,020$
(-)- 5 ¹⁶	R	-147	$[\theta]_{287} = -8560$ $[\theta]_{212} = -11,440$

^a All rotations were obtained in 95% ethanol solution. ^b Maximum (minimum) was not reached before optical cutoff for the instrument. ^c The CD and ORD determinations were obtained in ether.

were >90%¹² and the configurations were established with the modified octant rule.¹¹ The results obtained using (*R*)-**1b** are given in Scheme I. Photoepimerization does not occur at low conversion as demonstrated by the rotation of recovered **1b** but does become an important process in high conversion runs. When the photostationary mixture has been reached (~70 hr, 50% conversion) 72% racemization of both **1b** and **3b** was observed. Since this rearrangement is reversible and the starting ketone does not photoepimerize the racemization must be occurring either from **3b** in competition with the rearrangement back to **1b** or simply by a nonstereospecific rearrangement back to **1b**.¹³

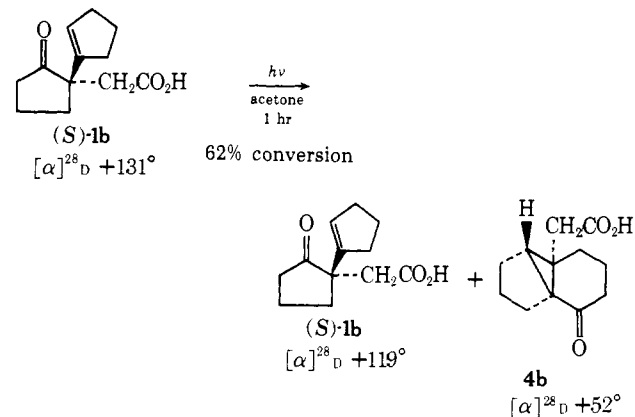
Scheme I



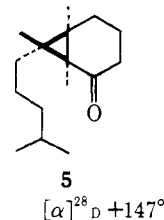
The acetone sensitized rearrangement of the enantiomers of **1b** was examined in detail. Each enantiomer was irradiated for varying periods of time, the product and starting ketone were separated, and each was analyzed for optical purity.¹² Scheme II gives the results of one such determination. Reactions in excess of 90% conversion gave **4b** with the same optical purity. Acetone sensitized irradiation did not

racemize or rearrange **4b** thus demonstrating its photostability.¹⁵

Scheme II

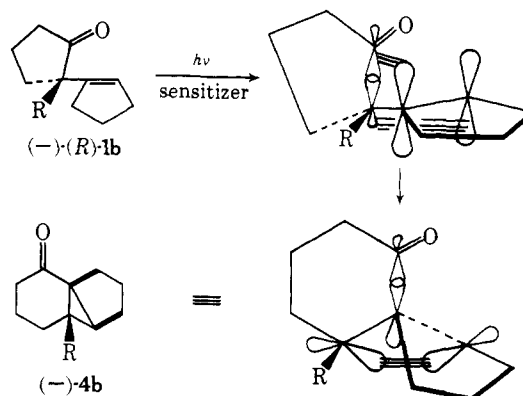


The determination of the absolute configuration of (+)-**4b**, crucial to the mechanistic picture for the oxa-di- π -methane reaction, was determined to be that shown in Scheme II by (1) use of the modified octant rule for cyclopropyl ketones^{16a} and (2) by comparison of the CD data of (+)-**4b** with that of (+)-**5**^{16b} (Table I).



The efficiencies for the reactions of **1a** were also measured. The direct irradiation occurs with a disappearance efficiency of $\Phi_d = 0.09$ and an appearance efficiency of $\Phi_a = 0.054$ (**3a**). In contrast, the sensitized rearrangement occurs with much higher efficiency; $\Phi_d = 0.35$ and $\Phi_a = 0.25$ (**4a**).

These results clearly show that for unhindered β,γ -unsaturated ketones the oxa-di- π -methane rearrangement occurs with *inversion* of configuration at the α -carbon (C-2). Interestingly, the same stereochemical consequence has been reported recently by Zimmerman for the di- π -methane rearrangement.¹⁷ Such a stereochemical consequence can occur for a rearrangement in which the excited state follows the allowed $\pi 2_a + \sigma 2_a$ pathway¹⁸ as shown in Scheme III. The acetone-sensitized excited triplet must rearrange with a multiplicity change ($T \rightarrow S$) before product is reached. Additional possible mechanisms based on (a) a preferred

Scheme III. The $\pi 2_a + \sigma 2_a$ Pathway for (-)-(R)-**1b**

ground state or excited state conformer or (b) a single, highly reactive conformer are less compelling from examination of molecular models and the observed stereospecificity of the rearrangement. Instead, the spin inversion may occur on the same single energy barrier surface which leads to product similar to that postulated for radiationless decay of excited benzene.¹⁹

Acknowledgments. Research grants from the National Institutes of Health (GM-16611) and the National Science Foundation (GP 38643) are gratefully acknowledged.

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- (9) Three of the four studies⁷ have been on steroid systems where axial methyl groups, the rigid steroid nucleus, or other sites of unsaturation may influence the rearrangement (see, for example, the discussion of ref 6). Of the concerted mechanisms, only the $\sigma_2a + \pi_2a$ is possible for **1** due to the restriction of the cyclic olefin, a feature of most of the known oxa-di- π -methane substrates.³ The other factors are absent.
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- (18) This may also be termed a $\pi_2a + \sigma_2a + \pi_2a$ rearrangement involving the carbonyl π -orbital, a necessary component of the oxa-di- π -methane rearrangement. Because the configuration about the carbonyl π -bond cannot be determined and for illustrative purposes, we have used the $\pi_2a + \sigma_2a$ diagram. (See also R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Academic Press, Germany, 1970, pp 96-97.)
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Polar Effects in Radical Reactions. II. Nucleophilic Character of the Undecyl Radical¹

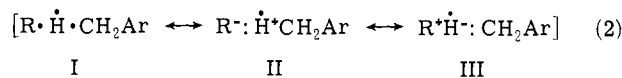
Sir:

Substituent effects on radical reactions are well known.²⁻⁹ In particular, Hammett ρ values have been mea-

sured for a variety of radicals in their attack on substituted toluenes (eq 1).^{8,9} These effects have been ascribed to the



resonance stabilization of the transition state by structures such as II and III. According to this model, those radicals for which form II is more important would exhibit electro-



I

II

III

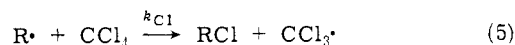
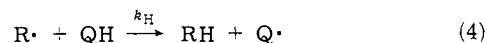
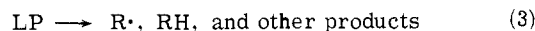
philic character, while those for which structure III is more significant would be nucleophilic. The absolute magnitude of the polar effect in either case would be dependent upon the reactivity of the particular radical.

Recently, an alternative rationalization of the data was proposed,¹⁰ one in which partial charge separation in the transition state is considered to be unimportant. It was postulated that ρ merely reflects differences in the bond dissociation energies of the benzylic hydrogens in the substituted toluenes and that the magnitude of ρ is a measure of the sensitivity of the abstracting radical to those differences. Unlike the other model, this treatment leads to the prediction that radicals are limited to negative (or zero) ρ values. As before, the size of ρ would be dependent upon radical reactivity.

A key test of the two models was provided by Pryor, Davis, and Stanley in their study of the *tert*-butyl radical.¹¹ A ρ value of 0.99 was found; this was the first positive ρ value reported for hydrogen abstraction from toluenes.

We have studied the 1-undecyl radical and here report the second positive ρ value observed for hydrogen abstraction from toluenes. This result provides additional support for the argument that radical reactions are susceptible to polar influences.

The undecyl radicals ($R\cdot$) were generated by thermolysis at 80° of *n*-lauroyl peroxide (LP) in a mixture of a toluene (QH) and carbon tetrachloride.^{12a} The equations for the reactions are as follows



Kinetic analysis of eq 3-5 leads to eq 6. Some RH is produced even when the peroxide is allowed to decompose in

$$\frac{[\text{RH}] - [\text{RH}]_0}{[\text{RCl}]} = \frac{k_H}{k_{C1}} \frac{[\text{QH}]}{[\text{CCl}_4]} \quad (6)$$

neat carbon tetrachloride. The concentration of RH was corrected for this material, designated $[\text{RH}]_0$. The k_H/k_{C1} values given in Table I were obtained from the slope of a plot of $([\text{RH}] - [\text{RH}]_0)/[\text{RCl}]$ vs. $[\text{QH}]/[\text{CCl}_4]$.¹³ A Hammett $\sigma\rho$ plot of the relative k_H values (see Figure 1) gives $\rho = 0.45 \pm 0.07$ ($r = 0.92^{14}$).¹⁵

A basic assumption in this derivation is that the only sources of RH and RCl are the reactions in eq 3-5.¹⁶ It has been observed that a chain sequence (eq 7 and 8) can occur in the CCl_4 system.^{12d} If the chain length is high, these reactions could produce appreciable levels of potential hydrogen and chlorine donors. We studied the CCl_4 -toluene

